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Phytolith-associated potassium in fern

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1 Phytolith-associated potassium in fern: Characterization, dissolution
2 properties and implications for slash-and-burn agriculture

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17

Abstract

In recent time, phytoliths (silicon deposition between plant cells) have been recognized as an important nutrient source for crops. The work presented here aims at highlighting the potential of phytolith occluded K pool in ferns. *Dicranopteris linearis* (*D. linearis*) is a common fern in the humid subtropical and tropical regions. Burning of the fern *D. linearis* is, in slash-and-burn regions, a common practice to prepare the soil before planting. We characterised the phytolith rich ash derived from the fern *D. linearis*, and phytolith associated potassium (K) (phytK), using X-ray tomographic microscopy in combination with kinetic batch experiments. *D. linearis* contains up to 3.9 g K kg⁻¹ d.wt, including K sub-compartmented in phytoliths. X-ray tomographic microscopy visualized an inter-embedding structure between organic matter and silica, particularly in leaves. Co-release of K and Si observed in the batch experiments confirmed that the dissolution of ash phytoliths is one of major factors controlling K release. Under heat treatment, a part of the K is made available, while the remainder entrapped into phytoliths (ca. 2.0 – 3.3%) is unavailable until the phytoliths are dissolved. By enhanced removal of organic phases, or forming more stable silica phases, heat treatment changes dissolution properties of the phytoliths, affecting K release for crops and soils. The maximum release of soluble K and Si, occurred from phytoliths treated at 500 - 800 °C. For quantitative approaches for the K provision of plants from the soil phytK pool in soils, factors regulating phytolith dissolution rate have to be considered.

Keywords: potassium; phytolith; fern; *Dicranopteris linearis*

Introduction

Dicranopteris linearis (*D. linearis*) is one of the most common ferns in the humid subtropical and tropical regions (Scott, 1969; Guariguata, 1990). *D. linearis* can tolerate low soil nutritional status, occurring on shallow, immature soils, mountain ridges, precipices or in

severely disturbed sites such as landslides, road-cuts and degraded forest lands (Scott, 1969; Guariguata, 1990), and plays an important role for ecological succession (Atkinson, 1970). It contains very low contents of nitrogen and phosphorus, but silicon (Si) and potassium (K) can be assimilated at significantly higher levels (Russell *et al.*, 1998; Amatangelo & Vitousek, 2008). While Si tends to be immobilized by polymerization, and subsequent precipitation in inter- and intracellular spaces of leaves and stems to form phytoliths (Piperno & Stothert, 2003; Parr & Sullivan, 2005; Mazumdar, 2011), K can be re-translocated to supply the appropriate ionic environment for metabolic processes throughout the plant (Leigh & Wyn Jones, 1984). We hypothesize that K can be sub-compartmented in organic matter associated, or even occluded, within the phytolith structure (phytK) during precipitation of Si. This means that this K pool is relatively unavailable for plant uptake even if the fern residue is returned to the soil and it is likely that K release is linked with the dissolution of phytoliths.

Overall, dissolution of phytoliths is controlled by the protonation, deprotonation, and hydrolysis of surface $\equiv\text{Si-OH}$ groups (Ehrlich *et al.*, 2010). This process occurs via nucleophilic attack (Dove & Crerar, 1990). pH is a crucial factor in phytolith dissolution, via protonation or deprotonation reactions (Frayse *et al.*, 2009; Nguyen *et al.*, 2014), which can either increase resistance of the surface or make the surface more vulnerable from nucleophilic attacks (Dove & Crerar, 1990). Deprotonation of the silanol groups (Si-OH) on the phytolith surface can facilitate hydrolysis of $\equiv\text{Si-O}^-$ bonds, which is known to be a first step for dissolution (Dove & Elston, 1992; Fraysse *et al.*, 2006). Adsorption of cations from aqueous solutions onto deprotonated $\equiv\text{Si-O}^-$ sites leads to polymerization (Weres *et al.*, 1981). Therefore, the surface of phytoliths is strengthened against dissolution. Associated organic matter (phytC) (Li *et al.*, 2014; Song *et al.*, 2016; Guo *et al.*, 2015), may be another factor in preserving phytoliths against hydrolysis, acting as a protective barrier (Parr & Sullivan, 2005; Nguyen *et al.*, 2014). PhytC can be lost upon burning, which is a common practice of field

preparation in the slash-and-burn farming. Little is known about the effect of heat treatment on phytC loss, surface property changes and dissolution rate of the fern *D. linearis* derived phytoliths.

Slash-and-burn farming is typical in upland north Vietnam, where *D. linearis* colonises soil that is left fallow. Slash and burn causes *D. linearis* phytolith-containing ash to be re-cycled to the soil, providing nutrients for subsequent crops. In this study, phytoliths obtained from ashing of fern *D. linearis* plants were used to examine release of Si and K and to investigate how heat interacts with the phytolith structure with respect to subsequent K dissolution.

Materials and methods

Phytoliths obtained from 300 - 1000 °C ashing were prepared. X-ray tomographic microscopy provided visualization of siliceous structure within the phytolith. Scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), specific surface area (SSA) and chemical composition analysis were carried out to evaluate transformation of phytoliths, and the effect of this transformation on Si and K release. The reactivity of biogenic silica is strictly related to changes in surficial properties (Cabanès and Shahack-Gross, 2015) and, in particular, loss of reactive surface sites. Therefore, surface charge (SC) was also determined as it is the key electrochemical parameter of the solid-liquid interface indicating ion adsorption, and ionization of surface functional groups, providing important information on dissolution kinetics (Walther, 1996). Other physio-chemical properties of the ashed samples, such as pH, electro-conductivity (EC) and organic carbon (OC), were determined to ascertain how they relate to phytolith dissolution.

Study site and sample production

D. linearis was collected from its natural habitat in a mountainous region (21°30' N, 104°47' E), with an elevation of ~1400 m, located in the Northwest of Vietnam (Fig. 1). The

soil is the Ferralic Acrisol which has developed on the basaltic rock. Slash-and-burn farming in this region has been practiced for hundreds of years, where maize is cultivated after burning. The average temperature is 23.5 °C, with an average relative humidity of 85%. Average annual precipitation is 1700 mm, fairly evenly distributed throughout the year. (Fig. 1)

D. linearis was collected by harvesting above ground biomass from three separate plots (1 m x 1 m). The samples were air-dried and 1.0 mm sieved. Elemental composition (Table 1) was determined by XRF spectroscopy (Rigaku, Nex CG). Ashing was conducted by heating 50 g of the sample, bulked from sampling plots, in a furnace at 300, 400, 500, 600, 700, 800, 900 and 1000 °C, for 2 h. Phytoliths were obtained from the ash by washing 3 times with deionized water, followed by centrifugation and decantation. The centrifugate phytoliths were dried at 60 °C for 24 h.

(Table 1)

Characterization of samples

The arrangement of Si and organic matter structures in dried stems and leaves of the *D. linearis* was examined by synchrotron-based X-ray tomographic microscopy, at the Swiss Light Source of the Paul-Scherrer-Institute in Villigen, Switzerland, using a 13 keV monochromatic beam at the TOMCAT (TOMographic Microscopy and Coherent rAdiology experimenTs) beamline. A sample was fixed on a centering and rotation stage in front of magnifying optics and a camera detector. A series of 2D radiographic images was acquired for different sample angular positions and subsequently tomographically reconstructed. A 3D-rendering was generated by using YaDiV software (Frieze *et al.*, 2013).

The chemical composition of *D. linearis*, and its ashes, was quantified by XRF (Rigaku, Nex CG). The total organic carbon (TOC) in the samples was measured by wet digestion with concentrated H₂SO₄ and 0.5 M K₂Cr₂O₇ at 170 - 180 °C. SEM-EDS using a

FESEM S-4800 (Hitachi Co., Tokyo, Japan) instrument, was used to map the distribution of elements in ashed sample phytoliths. The presence of crystalline phases in the ash samples was examined by powder X-ray diffraction (Bruker AXS D5005, Germany). The surface functional groups of the ash samples were identified by FTIR spectroscopy (Nicolet™ iS™5 FT-IR, Thermo Scientific, USA). The SSA of the samples was measured with a Gemini VII 2390p surface area analyzer.

Kinetic batch experiments

To examine K and Si solubility, each 100 mg of ash sample was mixed with 100 mL of deionized water in 125-mL plastic tubes. Suspensions were gently shaken and allowed to stand for 24 h at room temperature. For the samples pre-treated at 400 and 800 °C, the batch experiments were extended up to 7 d, with sampling at 24 h intervals. pH and EC were measured in aliquots of these suspensions by using a pH meter (Toledo, FE20, Switzerland) and an electrical conductivity meter (AD3000, ADWA, Hungary), before taking samples for quantification of Si and K release. The suspensions were passed through a 0.45 µm pore-size cellulose acetate filter. Soluble Si and K were determined using an ICP-MS iCap Q (Thermo Scientific, Bremen, Germany). All experiments were conducted in triplicates. Surface charge was quantified by polyelectrolyte titration in a particle-charge detector (PCD 05, Müttek, Herrsching, Germany). Suspensions were dispersed by an ultrasonic treatment for 15 s and then transferred into the titration cell. The titration with the polyelectrolyte was terminated at the point of zero charge where the electro-kinetic potential is zero.

Statistical analysis

The Pearson's test and multiple regression using SPSS 20.0 software, were used to examine the correlations between parameters. Principle components analysis (PCA) was also conducted, again in SPSS.

Results

Sample characterization

Tomographic images of leaf and stem phytoliths found high porosity, derived from longitudinal vascular bundles, veins or fibers in the stem (Fig. 2a) and leaf (Fig. 2d). Based on sample density, two phases of organic matter, colored with green (low density) and blue (high density), and Si-rich phase colored with pink, were detected. In the stem, limited Si-phase was observed (Fig. 2c), embedded into the high-density organic phase (lignin, cellulose) (Fig. 2b). In the leaf, the Si-phase tends to be more porous near the leaf surface (Fig. 2d and 2e), creating thin silica-rich layers (Fig. 2f), forming a protective cover for leaf veins, stabilized by silicified structures in inter- and intracellular spaces.

(Fig. 2)

Heat treatment of *D. linearis* led to significant changes in chemical composition and SSA (Table 2). When heating temperature changed from 300 to 1000 °C, OC decreased from 10.1 to 0.2%. The total Si and K contents of the unashed sample were 2.2 and 0.3%, respectively. The Si content changed from 8.7 to 15.4%, and K from 2.0 to 3.3%, between 300 to 1000 °C, respectively. The SSA increased from 42.5 to 161.2 m² g⁻¹ when the temperature changed from 300 to 700 °C. A step decrease in SSA occurred above 700 °C, decreasing to 5.4 m² g⁻¹ (Fig. 3). The SC ranged from -18.3 to -5.8 mmolc Kg⁻¹, decreasing for ashed samples. This might be related to the decreasing OC content at higher temperatures and to limited Si-OH represented on the surface as identified in Fig. 4b.

(Table 2)

(Fig. 3)

The XRD patterns of the phytolith-containing ash derived from different treatment temperatures are shown in Fig. 4a. At temperatures < 800 °C, no specific reflection peak was observed, suggesting that silica occurs in amorphous form. Temperatures above 800 °C can favor crystallization and cause the formation of more stable silicates, i.e., leucite and zeolite. Formation of zeolite might be a consequence of zeolization at high temperatures under the

presence of Si, Al, alkaline elements and internal water. Functional groups of the samples were revealed through FTIR spectra as described in Fig. 4b. The bands at $\sim 1100\text{ cm}^{-1}$ and 800 cm^{-1} , representing the stretching vibration of the SiO_4 tetrahedron and the bending vibration of inter-tetrahedral $\equiv\text{Si-O-Si}\equiv$ bonds, were apparent for almost all pretreatments. The band at $\sim 900\text{ cm}^{-1}$, linked to Si-O stretching vibration of $\equiv\text{Si-OH}$ groups, was missing at the temperatures $> 800\text{ }^\circ\text{C}$. The absence of this band at high temperatures might be due to transformation of $\equiv\text{Si-OH}$ to $\equiv\text{Si-O-Si}\equiv$ bonds.

(Fig. 4)

Solubility of Si and K

Dissolution kinetics

Releases of Si and K from samples derived from different treatment temperatures were reflected by significant concentration increases of soluble Si and K with time (Fig. 5a). While soluble K was significantly increased with time, less increase was observed for Si. After 7 d, Si and K releases were 5.2 and 17.2 mg L^{-1} for the $400\text{ }^\circ\text{C}$ -treated sample, 7.0 and 13.8 mg L^{-1} for the $800\text{ }^\circ\text{C}$ -treated sample, respectively. For both the 400 and $800\text{ }^\circ\text{C}$ -treated samples, K concentration showed a steep increase within the first 3 d, and minor releases after 3 days, while Si concentration in the supernatant continuously increased over the period of 7 d. Correlation coefficients obtained from the Pearson's test for samples treated at 400 and $800\text{ }^\circ\text{C}$ were 0.982 and 0.986 respectively, indicating a strong relation between released Si and K (Fig. 5b). A significant correlation at the 0.01 level for both the 400 and $800\text{ }^\circ\text{C}$ -treated samples is an obvious evidence for a strong relation between Si and K.

(Fig. 5)

Effect of treatment temperature

Solubility of Si and K in the phytoliths derived from *D. linearis* was highly affected by heating temperature (Fig. 6). In general, soluble concentrations of Si were almost lower

than those of K over the entire temperature range from 300 to 1000 °C. With a change in treatment temperature from 300 to 600 °C, an increase of the soluble Si and K from 1.0 to 2.1 mg L⁻¹, and 4.1 to 10.5 mg L⁻¹, respectively, was observed. At higher temperatures, 700 – 1000 °C, the solubility of Si and K severely decreased. Lowest values of soluble Si and K were 0.5 and 0.4 mg L⁻¹ for the sample treated at 1000 °C. Si and K solubility had similar trends (Fig. 6a), and with maxima between 500 – 800 °C. A scatter plot (Fig. 6b) shows the correlation between the released Si and K, with R² of 0.724.

(Fig. 6)

PC1 versus PC2 illustrated the differentiation between treatment temperature and released Si and K and other properties i.e. pH, EC, SSA, SC and OC (Fig. 7). The first PC showed positive values for all parameters except SC. The second PC was strongly associated to OC with positive effect and pH with negative effect, while lesser correlations were found for pH, SSA, EC and released Si and K. According to the ordination of variables in the PCA diagrams, released Si and K is associated with SSA, pH and EC rather than OC and SC. No correlation between the treatment temperatures at 300, 900 and 1000 °C and all variables occurred. Treatment temperature of 400 °C showed a trend to be associated with OC, whereas those of 600 to 800 °C tend to associate with SSA, pH and EC.

(Fig. 7)

Discussion

In plant tissues Si tends to be immobilized by polymerization, depositing in inter- and intracellular spaces to form phytoliths (Parr & Sullivan, 2005; Nguyen *et al.*, 2014). K is more mobile but can become entrapped within phytoliths. The 3D images obtained from X-ray tomographic microscopy revealed inter-embedding structures between organic matter and silica, particularly in leaf, in which the near-leaf-surface silica layers facilitate mechanical strength and decrease transpiration (Gong *et al.*, 2003; Chen *et al.*, 2011), though this was not

explored here. Observation of the inter-embedding structures of phytoliths suggests that precipitated silica can consolidate organic phases and sequester K. Micropores within silica phases (Mohamad Remli *et al.*, 2014) could contain some occluded organic compounds and K. Under heat treatment, organic phases can be removed, exposing phytolith silica. Morphology of the phytoliths might also be affected (Wu *et al.*, 2012; Evett & Cuthrell, 2017), with melting at high temperatures resulting in a re-arrangement and crystallization of silica, as deduced from XRD. Upon heating, losses of OC occurred, while K was enriched.

Solubility of Si increased as a result of phytolith desilification. A corresponding increase of the K concentration in the supernatants suggests a relationship between K and Si releases. This relationship was confirmed by scatter plots versus released Si with K (Fig. 6b). Therefore, K release is related to the dissolution of phytoliths. As K is released at a faster rate than Si (Fig. 6a), apart from K sequestered within phytoliths, K bound to organic matter, inter-embedded with phytoliths, was also released on organic matter thermal decomposition, as described by Trinh *et al.* (2017). The release of K from organic matter is likely to attribute to the higher dissolution rate of K over Si. The temperature of the sample treatment may also be a factor regulating phytolith desilification and K release. The maximum values of soluble Si and K were observed from 500 till 800 °C, whereas lower dissolution was found at < 500 °C or > 800 °C. Heat treatment changed surface properties of the phytoliths, thereby affecting solubility of Si and K. The ordination of variables in the PCA diagrams showed that pH and SSA are factors favoring Si and K releases, whereas SC and OC have contrary effects. High organic matter content of lower temperature (< 500 °C) treated samples prohibited Si and K release because its coating made the phytolith surface more resistant to dissolution (Van Cappellen *et al.*, 2002; Parr & Sullivan, 2005). With increasing temperature, dehydroxylation of silanol groups results in more siloxane bonds and the surface becomes hydrophobic (Zhuravlev, 2000). This reaction reduces adsorption of water molecules on the surface and

prevents the breakage of the surface siloxane bonds. It can therefore explain why less Si and K were released from the phytolith samples in this case at higher temperatures. In addition, the formation of stable silica at high temperatures ($> 800^{\circ}\text{C}$) resulted in a product with low specific surface area and less activity (Kordatos *et al.*, 2008; Nguyen *et al.*, 2014), likely also resulting in a decrease of Si and K release.

The XRD patterns indicate newly-formed crystals, leucite and zeolite, in the temperature range from 900 - 1000 $^{\circ}\text{C}$. Occurrence of zeolite observed at high temperatures was not expected since zeolite is usually formed under hydrothermal conditions (Cundy & Cox, 2005). The occurrence of alkaline elements (data not shown) in combination with structural water under high temperature might be initial for the nucleation from which Si and Al can be polymerized to build up zeolite crystals. The newly-formed nano-size particles observed on the surface (Fig. 3c) were an evidence of partial melting and re-crystallization processes on the surface of phytoliths. The effect of “neo-formed” zeolite upon the releases of Si and K, however, was not in focus of this study.

Implications for the soil system and options for management

This study relates to a more detailed understanding regarding the K pool in ferns and its release properties, with the findings applicable to soil nutrient management for slash-and-burn agriculture in many upland regions. Fern *D. linearis* contains up to 3.2 g K kg^{-1} , suggesting that this K pool can be an additional source for soils and crops. Under heat treatment, a portion of the K is readily soluble, whereas the remaining part is tightly associated with phytoliths, thereby being unavailable until the phytoliths are dissolved. Co-release of K and Si on heat treatment was observed in batch incubation experiments, confirming dissolution of the phytoliths as one of the main factors controlling K release. The heating temperature could affect K and Si releases by intensifying the removal of occluded organic matter or crystallizing the silica surface of the phytoliths. The maximum values of soluble K and Si

release were observed in the 500 - 800 °C treatments, which suggests that the preheat-treatment of the fern *D. linearis* at this temperature range is optimal toward serving as a fast available K source for crops and soils. At temperatures above 900 °C, the newly-formed crystals i.e. leucite and zeolite were identified in the ashes, but their occurrence and to what extent they can affect release of K, remains unclear. Phytoliths and their phytK, when embedded into soils, are affected by various physico-chemical factors, which govern phytolith dissolution and hereby K release to plants. Quantity values indicating the size of the soil phytK pool in relation to soil properties, however, are beyond the scope of this work. They will be subject of a future study employing percolation experiments.

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- 351

Table captions

Table 1. Chemical composition of the *D. linearis* above ground biomass, mean values with standard deviations in brackets.

Table 2. pH, specific surface area (SSA), surface charge (SC), electrical conductivity (EC), organic carbon (OC), Si and K content of the fern plant ash samples obtained from 300 to 1000 °C treatment.

Figure captions

Figure 1. Fern *D. linearis* collected from the study site at a mountainous area in the northwest Vietnam.

Figure 2. Tomographic images revealing the location of Si phytolith phase in fern *D. linearis*: cross-section (a), 3D view (b) and 3D view with only Si separated (c) of the stem; and cross-section (d), 3D view (e) and 3D view with only Si separated (f) of the leaf. Phytolith Si-rich phase is coloured pink, high-density organic phase is coloured with blue, and low-density organic phase coloured with green.

Figure 3. SEM images of the ash phytoliths derived from heat treatments at 700 °C (a), 1000 °C (b), granules formed on the surface of ash treated at 1000 °C (c), and EDS spectra of ashes treated at 700 °C (d) and 1000 °C (e).

Figure 4. XRD patterns (a) and IR spectra (b) of ashed fern *D. linearis* samples in the temperature range from 300 - 1000 °C.

Figure 5. Releases of Si and K from *D. linearis* ash samples treated at 400 and 800 °C in a time sequence up to 7 d (a), and their correlation (b). Data points represent mean values with standard errors for 3 replicates. Error bars might be smaller than the symbol size.

Figure 6. Dependence of the solubility of Si and K from *D. linearis* ashes on treatment temperature.

377 Figure 7. Score plots of PC1 versus PC2 indicating the differentiation of treatment
378 temperature and soluble K and Si, pH, electrical conductivity (EC), organic carbon (OC),
379 surface charge (SC) and specific surface area (SSA) for ash phytoliths.